Urban Organic Aerosols Measured by Single Particle Mass Spectrometry in the Megacity of London

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ABSTRACT

During the month of October 2006, as part of the REPARTEE-I experiment (Regent's Park and Tower Environmental Experiment) an Aerosol Time-Of-Flight Mass Spectrometer (ATOFMS) was deployed at an urban background location in the city of London, UK. Fifteen particle types were classified, some of which were accompanied by Aerosol Mass Spectrometer (AMS) quantitative aerosol mass loading measurements (Dall'Osto et al., 2009a,b). In this manuscript the origins and properties of four particle types postulated to be due to locally generated aerosols, independent of the air mass type advected into London, are examined. One particle type, originating from lubricating oil (referred to as Ca-EC), was associated with morning rush hour traffic emissions. A second particle type, composed of both inorganic and organic species (called Na-EC-OC), was found enhanced in particle number concentration during evening time periods, and is likely to originate from a source operating at this time of day, or more probably from condensation of semi-volatile species. A third class, internally mixed with organic carbon and sulphate (called OC), was found to spike both in the morning and evenings. The fourth class (SOA-PAH) exhibited maximum frequency during the warmest part of the day, and a number of factors point towards secondary aerosol production from traffic related volatile aromatic compounds. Single particle mass spectra of this particle type showed an oxidized polycyclic aromatic compound signature. Finally, a comparison of ATOFMS particle class data is made with factors obtained by Positive Matrix Factorization from AMS data.. Both the Ca-EC and OC particle types correlate with the AMS HOA primary organic fraction (R^2 = 0.65 and 0.50 respectively), and Na-EC-OC, but not SOA-PAH, which correlates weakly with the AMS OOA secondary organic aerosol factor (R^2 = 0.35). A detailed analysis was conducted to identify ATOFMS particle type(s) representative of the AMS COA cooking aerosol factor, but no convincing associations were found.

1. INTRODUCTION

Tropospheric particles contain a significant and variable fraction of organic material, ranging from 20% to 90% of the fine particulate mass (Kanakidou et al., 2005) and divide into two broad categories termed primary and secondary. Primary organic aerosols detected in urban areas are mainly directly emitted from combustion sources, including heavy and light duty vehicles, wood smoke, cooking activities, industries and many others. Once primary particles are emitted they are modified in the presence of various atmospheric oxidants, yielding secondary organic aerosols (SOA) with distinctly different chemical and physical properties compared to their precursor primary particles (Donahue et al., 2009).

SOA is also formed from reactions of volatile organic compounds (VOC). SOA consists of a mixture of oxygenated organic species dependent on the degree of processing of the aerosol in the atmosphere, and the precise mechanisms of formation and evolution of SOA are still highly uncertain (Hallquist et al. 2009). The sources and the production mechanisms of primary and secondary organic aerosols represent one of the biggest uncertainties in aerosol science. Models informed by chamber experiments do not always capture the variability of observed SOA loadings, and often predict far less SOA than is observed (Hallquist et al. 2009).. This underestimation of SOA strongly suggests the importance of additional pathways of SOA formation not typically studied in laboratory experiments or included in models (Zhang et al. 2007). The chemistry of the formation and continuing transformation of low-volatility species in the atmosphere has been the subject of recent review articles (Kanakidou et al., 2005; Goldstein and Galbally, 2007; Kroll and Seinfeld, 2008). Until recently, organic particulate material was simply classified as either primary or secondary with the primary component being treated in models as nonvolatile and inert. However, the simplified models failed to explain a number of key aspect of the aerosols, including the highly oxygenated nature of ambient OA and the high concentrations of OA during periods of high photochemical activity. Recent studies have shown that semi-volatile components of primary aerosols desorb into the gas phase during aerosol transport, thereby undergoing oxidation in the gas phase, leading to SOA formation (Robinson et al., 2007). This opens the possibility that low-volatility gas-phase precursors, including long chain n-alkanes, PAHs and large olefins, are a potentially large source of SOA.

Polycyclic Aromatic Hydrocarbons (PAH) have been identified as a major component in emissions from diesel engines and wood burning sources (Schauer et al., 1999; 2001). The photo-oxidation of these compounds has been shown to yield high molecular weight (MW) oxygenated compounds (Sasaki et al., 1997; Bunce et al., 1997; Wang et al., 2007), which can partition into the particle phase and lead to significant SOA formation (Mihele et al., 2002). Current atmospheric models do not normally include secondary organic aerosol (SOA) production from gas-phase reactions of polycyclic aromatic hydrocarbons (PAHs). Chan et (2009) reported a laboratory study of secondary organic aerosol formation from photooxidation of naphthalene and alkylnaphthalenes. Although the gas-phase emissions were dominated by low molecular weight aromatics, these compounds were estimated to account for only 14% of the SOA formed in first 3 h of photooxidation. The estimate is consistent with laboratory results of photooxidation of diesel exhaust (Robinson et al., 2007), in which the “known” consisting primarily of single-ring aromatics gas phase precursors, account for at most 15% of the SOA formed. The contribution of PAH to SOA is still significant after 12 h of oxidation, at which point the SOA from PAH is about twice that from light aromatics (Chan et al., 2009).

Whilst biogenic precursors (predominantly monoterpenes) have traditionally been thought to dominate regional SOA formation, anthropogenic compounds may contribute an appreciable fraction of SOA in urban areas. Mono-aromatic hydrocarbons are one of the most abundant types of organic compound found in the urban atmosphere. Langford et al. (2010) recently reported fluxes and concentrations of volatile organic compounds above central London, estimating that traffic activity was responsible for about 70% of the aromatic compound fluxes. The ultimate photo-oxidation products of many relatively simple mono-aromatic species remain unknown, due to the complexity and low concentrations formed. The incorporation of a mono-aromatic compound into polymeric compounds with acetal polymers was also suggested (Kalberer et al., 2004).

In recent years aerosol mass spectrometry has become available as a powerful tool for the on-line chemical characterization of individual aerosol particles (Murphy, 2007) or small aerosol ensembles (Canagaratna et al., 2007). During the month of October 2006, the REPARTEE-I campaign (Regent's Park and Tower Environmental Experiment) studied atmospheric chemical processes, and particularly those affecting atmospheric aerosol, in London. Two different particle mass spectrometers were deployed: an Aerodyne Compact Time-of-Flight Aerosol Mass Spectrometer (C-ToF-AMS) (Drewnick et al., 2005) and an Aerosol Time-of-Flight Mass Spectrometer (ATOFMS) (Gard et al., 1997). The ATOFMS provides single particle information on the abundance of different types of aerosol particles as a function of particle size with high time resolution, whereas the AMS measures quantitatively mass concentrations of the non-refractory aerosol components as well as species-resolved size distributions (Canagaratna et al., 2007).

These types of on-line aerosol analysis instrumentation have greatly advanced our understanding of atmospheric chemistry and climate (Sullivan and Prather, 2005). Whilst the AMS has provided advances in the source apportionment of primary versus secondary organic aerosol components (Canagaratna et al., 2007), the ATOFMS has less adequate source apportionment capabilities due to the difficulties in quantification of its outputs. However, as a main objective of this study, we investigate the temporal trends and the mass spectral features of specific particle types classified with the ATOFMS and we try to deduce chemical and physical aerosol features, attempt a source identification and compare the results with those obtained by using an AMS deployed during the same field study (Allan et al. 2010).

A number of papers generated during the REPARTEE experiment have already been published. During the REPARTEE-I field study for example, the ATOFMS focused on atmospheric chemical processes (Dall'Osto et al 2009a, b). Dall'Osto et al. (2009a) found two types of nitrate-containing aerosols: the first (33.6% of particles by number) appeared to be locally produced in urban locations during nighttime, whilst the second (22.8% of particles by number) was regionally transported from continental Europe. Dall'Osto et al. (2009b) reported on aerosol formation processes during a fog event within the campaign period. By applying Positive Matrix Factorization (PMF) on the organic AMS matrix, Allan et al. (2010a) reported a detailed source apportionment analysis of the organic aerosols. In summary, three OA contributions were identified in REPARTEE I: secondary Oxygenated Organic Aerosols (OOA, 53%), primary Hydrocarbon-like Organic Aerosol (HOA, 25%) and primary Cooking Organic Aerosol (COA, 22%) but a comparison with the ATOFMS results was not attempted. Table 1 summarizes the 15 clusters found during the REPARTEE I field study. Twelve of the 15 clusters contained mass spectral peaks characteristic of organic containing aerosols, accounting for 83.7% of the total particles classified (see Table 1). Of these, the 3 main clusters were associated also with nitrate aerosol and are already discussed in Dall'Osto et al. (2009a). Two specific ATOFMS clusters associated with secondary organic aerosol production during a fog event have already been discussed in Dall'Osto et al. (2009b). The present study aims to present a detailed analysis of some specific ATOFMS particle classes not described in other studies. The particle types herein described were predominantly organic particle types presenting systematic diurnal trends persisting over three weeks and therefore attributable to local primary and secondary processes occurring daily at the local scale and independent of whichever air mass type the city of London was exposed to. Aspects of the data are compared with the source attribution results for organic carbon derived from PMF analysis of AMS data collected during the same campaign by Allan et al. (2010a,b).

The ATOFMS collects individual particles whilst the AMS collects an ensemble of particles which can be interpreted as a mass concentration of the major non-refractory components. The AMS thus measures the particle mass loading ($\mu g\ m^{-3}$) whilst the ATOFMS temporal trend is reported as the number of particles detected (ATOFMS counts per hour), but the correlation can be very good ($R^2=0.75$) (Dall'Osto et al., 2009a). This study does not aim to look at general organic and inorganic components, but aims to present specific four organic particle types occurring during this study, which have not been reported in our earlier papers (Dall'Osto et al., 2009 a,b).

2. EXPERIMENTAL

2.1 Aerosol sampling

Sampling took place in Regents Park, one of the Royal Parks of London between 4th and 23rd October 2006. Regents Park is located in the northern part of central London. The park has an outer ring road called the Outer Circle (4.3 km) and an inner ring road called the Inner Circle. Apart from two link roads between these two, the park is reserved for pedestrians and the ca. 2 km^2 park is mainly open parkland. The sampling site chosen was inside the inner circle, in an open area usually reserved for parking and gardening purposes. All the instruments were housed in a mobile laboratory. The site was operated as part of the REPARTEE-I experiment (Regent's Park and Tower Environmental Experiment) aiming to study atmospheric chemical processes, and particularly those affecting atmospheric aerosol, in London (Harrison et al. 2011). Meteorological, gas-phase and aerosol measurements were conducted from the top of a 10 m high tower constructed on site. To minimise sampling losses, aerosol was drawn down a sampling stack from which it was iso-kinetically sub-sampled into a 2 cm diameter stainless steel tube leading to the mobile laboratory. Local meteorological conditions were measured by humidity and temperature probes, and a sonic anemometer which measured the 3-D wind field at the sampling site.

2.2 Instrumentation

The ATOFMS collects bipolar mass spectra of individual aerosol particles. Ambient aerosol is focused into a narrow particle beam for sizes between 100 nm and 3 µm. Using a 2-laser velocimeter particle sizes are determined from particle velocity after acceleration into the vacuum. In addition, the light scattered by the particles is used to trigger a pulsed high power desorption and ionization laser (λ=266 nm, about 1 mJ/pulse) which evaporates and ionizes the particle in the centre of the ion source of a bipolar reflectron ToF-MS. Thus, a positive and negative ion spectrum of a single particle are obtained. The mass spectrum is qualitative in that the intensities of the mass spectral peaks are not directly proportional to the component mass but are dependent on the particle matrix, the coupling between the laser and the particle and the shot to shot variability of the laser. However, the ATOFMS can provide quantitative information on particle number as a function of composition; providing a measure of all particle components and can be used to assess mixing state. The ATOFMS provides information on the abundance of different types of aerosol particles as a function of particle size with high time resolution (Gard et al., 1997). Recent studies (Jeong et al. 2011) report excellent correlations between inorganic species (sulphate, nitrate and ammonium) and total organic and elemental carbon detected with ATOFMS and other instruments such as the AMS, the Gas-Particle Ion Chromatograph (GPIC), and the Sunset Lab field OCEC analyzer. However, there are no intercomparisons between specific PMF factors derived from the AMS organic matrix (Ulbrich et al, 2009; Allan et al. 2010) and ATOFMS clustering results.

ATOFMS laser desorption/ionization of chemical species in the particles is accomplished using a Nd:YAG laser operating at 266 nm, and PAHs and their heterocyclic analogues present very high molar absorptivity at this wavelength therefore it is expected that these compounds will be detected among the most easily of all compounds using ATOFMS. The laser fluence of the LDI laser of the ATOFMS was kept very low (0.8- 0.9 mJ per pulse) in comparison to other studies (1.3-1.6 mJ). The reason for selecting lower laser fluence was to reduce the fragmentation of organic compounds, hence enhancing the detection of high molecular weight species as molecular ions (Silva and Prather, 2000). As a result, a wider variety of particle mass spectra is generated and can provide a better understanding of the different sources and processes occurring in the urban atmosphere.

A Multi-Angle Absorption Photometer (MAAP, Thermo Electron) (Petzold and Schonlinner, 2004) was also used to measure 1-minute averages of the ambient black carbon concentrations. Moreover, Dichotomous Partisol-Plus Model 2025 sequential air samplers, fitted with PM10 inlets were deployed for collecting fine ($PM_{2.5}$) and coarse ($PM_{2.5-10}$) fractions. A number of other instruments were used during the REPARTEE-I campaign but are not listed here since their data are not discussed in this paper. Local meteorology was determined by a Weather Transmitter WXT510 (Vaisala Ltd, Birmingham) probe. Gas measurements were obtained by Thermo Environment 42CTL chemiluminescence gas analyser with thermal converter and by Thermo Environment 49C photometric UV analyzer for NO_x and ozone, respectively.

2.3 Data analysis

The ATOFMS was deployed at Regents Park for 19 days, between 04/10/06 at 17:00 and 22/10/06 at 23:00. In total, 153595 particles were hit by the ATOFMS. The TSI ATOFMS dataset was imported into YAADA (Yet Another ATOFMS Data Analyzer) and single particle mass spectra were grouped with Adaptive Resonance Theory neural network, ART-2a (Song et al., 1999). The parameters used for ART-2a in this experiment were: learning rate 0.05, vigilance factor 0.85, and iterations 20. Further details of the parameters can be found elsewhere (Dall'Osto and Harrison, 2006). An ART-2a area matrix (AM) of a particle cluster represents the average intensity for each m/z value for all particles within a group. An ART-2a AM therefore reflects the typical mass spectrum of the particles within a group. The ART-2a algorithm generated 306 clusters used to describe the dataset. By manually merging similar clusters (Dall'Osto and Harrison, 2006), the total number of clusters describing the whole database was reduced to 15. Throughout this paper, an ATOFMS particle type is synonymous with an ATOFMS cluster. It is important to stress the fact that whilst the ATOFMS provides important information on the mixing state of the aerosols and temporal trends of unique particle types over time, the total number of particles sampled by the instrument does not have quantitative meaning without extensive calibrations as it is biased by transmission efficiency (Dall'Osto et al., 2006). Whilst some semi-quantitative ATOFMS measurements have been reported (i.e. Qin et al., 2006) in the literature, no attempt was herein tried to scale ATOFMS measurements with other instruments.

3. RESULTS

This paper focuses on four particle types named Ca-EC (Calcium – Elemental Carbon), OC (Organic Carbon), Na-EC-OC (Sodium – Elemental Carbon – Organic Carbon) and SOA-PAH (Secondary Organic Aerosols – Polycyclic Aromatic Hydrocarbons) accounting for 4.3%, 3.6%, 1.7% and 2.2% (respectively) of the ATOFMS particles classified during the REPARTEE I experiment.

The weather during the field study was characterized by unusually warm conditions for the month of October in the UK (average temperature 14.1±2.8C, relative humidity 82.6±10.7%; mean ±1 s.d. of hourly data). The predominant origin of air masses arriving at the receptor was westerly, with Atlantic air masses not strongly influenced by anthropogenic pollution. However, during two periods, air masses arriving at our site from mainland Europe (mainly France and Poland) were detected on 10–11 October 2006 and on 14–20 October 2006. Local wind direction roses were calculated for all 15 ATOFMS clusters, and ATOFMS particle types associated with regional and continental aerosols were found to be associated predominantly with an easterly origin. ATOFMS particle types characterized by daily diurnal profiles were mainly associated with south and east directions, where main roads bordering the Regents Park are located.

3.1 ATOFMS characterization

3.1.1 *ATOFMS mass spectra*

The positive and negative ART-2a AMs for the four particle types described are presented in Figure 1. The mass spectra of cluster Ca-EC (Figure 1a) show a strong signature due to calcium (m/z 40, 56, 57 and 96), EC (m/z -36, -48, -60) and OC (m/z 27, 29, 43). Strong signals in the negative mass spectrum are associated with nitrate (m/z -46, -62), whereas sulphate (m/z -97) is almost absent. This is consistent with a source in vehicle exhaust, which is rich in NO_x but depleted in SO_2 due to use of low sulphur fuel. This particle type has previously been associated with combusted lubricating oil emitted by traffic (Spencer et al., 2006; Toner et. al 2007) and consistently called Ca-EC although in this REPARTEE study a higher signal of nitrate is seen in the negative spectra (Fig. 1a).

Figure 1b shows the ART-2a AMs for cluster OC: strong signals due to organic fragments are seen at m/z 27, 29, 43, 51, 57 and 63. This particle, by contrast with the Ca-EC type, is internally mixed with both nitrate and sulphate, with a higher signal for the latter. Cluster Na-EC-OC (Figure 1c) shows a signal at m/z 23 for the inorganic component sodium, not seen in other mass spectra presented in Figure 1 and suggesting a different source. Moreover, beside the OC and EC component associated with the Na-EC-OC particle type, the negative spectra of this particle type also show signals due to inorganic nitrogen (m/z -26 [CN] and m/z -42 [CNO]), also not seen clearly in the other particle types.

Cluster SOA-PAH presents a unique positive mass spectrum (Figure 1d), with strong peaks at m/z 27 $[C_2H_3]^+$ and m/z 43 $[(CH_3)CO]^+$. M/z 51 $[C_4H_3]^+$, 63 $[C_5H_3]^+$, 77 $[C_6H_5]^+$ and 91 $[C_7H_7]^+$ are indicative of a strong aromatic signature (McLafferty, 1993). In the positive mass spectrum, the major peaks at m/z above 100 amu show a series at m/z 115, 128, 141, 152, 165, 178, 189, 202, 215, 226, 239 and 252 which is usually attributed to PAH compounds (Gross et al., 2000; Silva and Prather, 2000). Figure 2 shows positive and negative mass spectra of a single particle (aerodynamic diameter 400 nm) belonging to the ATOFMS particle type SOA-PAH. Additional peaks at m/z 180, 194, 208, 222, 236, 262 and 276, characteristic of oligomeric species with saturated carbon skeletons separated by Δ14 are present in addition to the PAH series separated by Δ13. Other peaks at m/z above 100 can be clearly seen with a series at m/z 105, 119, 133 and 147, possibly associated with benzoyl groups and unsaturated or cyclic phenoxy moieties (McLafferty, 1993). The peaks at m/z 69, 81 and 95 (particularly the strong peak at m/z 95) may represent the exo-sulphur aromatic series (sulphur attached to an aromatic ring) (McLafferty, 1993).

The single particle ATOFMS negative mass spectrum of cluster SOA-PAH (Figure 2) is dominated by m/z -25 and m/z -26 (likely to be $[C_2H]^-$ and $[C_2H_2]^-$ respectively) and m/z at -49 and m/z -73 (often found strongly correlated and likely to be related by an unknown fragmentation pattern), which are often associated with fragmentation of PAH and unsaturated organic compounds (Silva and Prather, 2000; Spencer et al., 2006). The presence of strongly acidic compounds is indicated by peaks in the negative spectra. Along with the common peak at m/z -97 $[HSO_4]^-$, peaks at m/z -80 $[SO_3]^-$, m/z -81 $[HSO_3]^-$ and m/z -64 $[SO_2]^-$ can be seen. The peak at m/z -81 suggests the particle is highly acidic (Whiteaker and Prather, 2003). It is interesting to note the minor presence of common peaks due to nitrate (i.e. m/z -46 $[NO_2]^-$, m/z -62 $[NO_3]^-$ and m/z -125 $[H(NO_3)_2]^-$. Perhaps the most interesting feature of the negative mass spectrum of Figure 2 is the presence of other oxygenated aromatic rings indicated by peaks not reported before in ATOFMS mass spectral characterization seen at m/z -107, m/z -121 and m/z -137, characteristic of fragmentation patterns often associated with flavonoids (Cuyckens and Claeys, 2004; Maul et al., 2008). By querying the whole ATOFMS dataset (about

150,000 single particle mass spectra), it was found that m/z -107, m/z -121 and m/z -137 were unique to this particle type. In summary, the positive and negative ATOFMS mass spectra of particle type SOA-PAH indicate a highly oxidised organic aerosol component internally mixed with acid sulphate species, along with a complex signature at higher m/z which is attributable to high molecular weight polyaromatic compounds.

3.1.2 *ATOFMS size distributions*

ATOFMS size distributions were obtained by scaling the ATOFMS particle number counts with particle number size distributions to calibrate inlet efficiencies (Qin et al., 2006). It should be stressed that the size distributions presented in this work have only semi-quantitative meaning, as the ATOFMS efficiency is different for different particles and each broad type of particles exhibits a different hit rate (Dall'Osto et al., 2006, Reinard et al., 2007). Whilst the ATOFMS measures precisely the vacuum aerodynamic diameter of individual particles (0.01μm resolution), particles were summed between 200nm and 3500nm at 100nm intervals for simplification. Figure 3 shows the size distributions for the four ATOFMS particle types Ca-EC, OC, Na-EC-OC and SOA-PAH. Clusters Ca-EC and OC show a uni-modal distributions peaking in the smallest detectable ATOFMS particle diameter at about 200nm. Previous ATOFMS findings point to primary combustion particles peaking at the smallest detectable ATOFMS particle diameter, whilst more aged secondary organic components (i.e. long range transport organic aerosol) are more typically distributed in the accumulation mode at around 500nm (Sullivan and Prather, 2005). The mass spectra of these two particle types described in section 3.1.1, along with the size distributions herein presented, suggestive of a primary origin of these particles.

Cluster Na-EC-OC also shows a mode peaking at the smallest sizes, but much less pronounced relative to clusters Ca-EC and OC. By contrast to the first three clusters presented so far, cluster SOA-PAH shows a mode peaking at about 350nm and not peaking at the smallest detectable ATOFMS particle diameter. The coarser mode of cluster SOA-PAH relative to clusters Ca-EC and OC suggests a different origin not related to primary emissions.

3.2. Time trend analysis

3.2.1 *Overview of the temporal trends*

The temporal trends (3 hours resolution) of the four ATOFMS clusters are presented in Figure 4. Clusters Ca-EC and OC (Figure 4a) showed maximum abundance during the morning of 13th October 2006, when low wind speed was associated with stagnant conditions, also reflected in high concentrations of primary traffic related species (BC, NO, NO_x, Figure 4b). Figure 4c shows the temporal profiles of the 3 PMF factor components of the AMS organic matrices described in Allan et al. (2010a). The AMS OOA component dominated the periods of 9th-10th and 14th-20th October 2006 affected by continentally influenced air masses, in which the ATOFMS showed nitrate internally mixed with elemental carbon and organic carbon (Dall'Osto et al., 2009a). AMS factor HOA shows its maximum on the morning of 13th October, and other high concentrations during the morning rush hours of 11th, 12th, 16th and 17th October, correlating with the maximum values of ATOFMS cluster Ca-EC related to primary traffic emissions (Figure 4a-c). The highest concentrations of cluster SOA-PAH (Figure 4a) occurred on 11th and 17th-20th October, which are also the days where AMS cluster COA presents its higher mass loading concentrations during daytime (Figure 4c).

3.2.2 *Diurnal profiles*

The temporal trends derived from a number of other instruments appear in Figure 5, showing the average diurnal profiles of (a)ATOFMS clusters described in Figure 1, (b) AMS PMF factors as reported in Allan et al. (2010a); (c) ozone, NO_x and BC concentrations; (d) relative humidity and temperature and (e) ATOFMS hit particles with m/z 55 (peak height > 100). ATOFMS Cluster Ca-EC, as expected from its mass spectra and size distribution, exhibits a maximum during morning rush hours (05:00-09:00) due to primary traffic emissions (Figure 5a). It shows the same traffic rush hours peaks as NO_x and BC (Figure 5c), along with the primary organic aerosol traffic related HOA (Figure 5b) derived by the AMS (Allan et al., 2010a). During rush hours BC concentrations were around 4 µg m^{-3}, NO_x concentrations about 20 ppb, and HOA about 1.5 µg m^{-3}. A second peak at about 16:00 due to the second traffic rush hour period is evident in Figure 5 from the ATOFMS cluster Ca-EC and NO_x diurnal trends. Cluster OC (Figure 5a) also showed a spike in the morning traffic rush hour, reflected by a good correlation with cluster Ca-EC ($R^2 = 0.7$). However, cluster OC also exhibited a second sharper peak during evening hours spiking at about 21:00. Cluster Na-EC-OC did not show as strong a diurnal profile as the previous classes described (Figure 5a) but a two fold increase occurred between 18:00 and 24:00 relative to the other hours of the day suggesting an additional evening aerosol source or atmospheric process responsible for this particle type. Figure 5a shows that in contrast to the other three ATOFMS particle types presented so far, ATOFMS particle type SOA-PAH exhibits a peak in the middle of the day. This cluster exhibits a bimodal daily trend: the earlier mode starts at about 08:00, as temperature also rises (Figure 5d) and lasts for about 3 hours. The second mode, peaking at 12:00 and 13:00 is in the hottest part of the day. Concentrations decrease substantially after 14:00, disappearing by about 19:00 (Figure 5a).

The diurnal profile of particles detected by the ATOFMS containing a peak with significant signal (peak height>100) at m/z 55 (Figure 5d) is also shown but is discussed in Section 4.

3.2.3 *Weekday-weekend trend*

Average mean values (± 1 standard deviation) of the weekday-weekend (WD-WE) variation was performed on all 15 clusters derived from the ca- 150,000 single particles detected during the REPARTEE-I campaign. The two clusters with the highest weekday to weekend ratio were found to be cluster Ca-EC (weekdays: 16±15; weekend: 8±6; average ATOFMS counts/hour) and cluster SOA-PAH (15±25; 3±7). Whilst clusters Ca-EC and cluster SOA-PAH were found to be two independent groups significantly different from one another (t-test, 95% confidence), cluster OC (12±17, 9±7) and cluster Na-EC-OC (4±3, 4±5) did not show any statistically significant WD-WE oscillation. A WD-WE analysis of other measurements was also performed in order to compare them with the variation of the ATOFMS clusters. An analysis of the particulate mass loading available for 3 different sites within London during the REPARTEE I campaign (park site "Regents Park" - RP, road site "Marylebone Road" - MR - and 160 metre tower "BT tower" - BT -, see Harrison et al., 2011) was carried out, but 16th October 2006 was removed as it exceeded 50 μg m^{-3} largely due to regional pollutant transport and was not comparable with the other days of the month of October 2006. $PM_{2.5}$ at the Marylebone Road air monitoring site showed a strong WD-WE variation (26±7, 20±7; μg m^{-3}, significantly different – t-test, 95%), whereas the background sites of RP (10±6, 10±7) and BT (10±8, 10.5±9) showed similar values for weekdays and weekend. However, whilst $PM_{2.5}$ at RP did not show a WD-WE variation, traffic markers showed a strong gradient between WD and WE periods (all statistically different, t-test 95%), including BC (3.2±1.7, 1.8±0.9; μg m^{-3}), NO (36±52, 9±14) and NO_x (70±54, 35±22). A brief analysis of the primary organic aerosol components described in detail in Allan et al. (2010a) showed the traffic HOA component to present a strong WD-WE difference: 1.3±0.8 μg m^{-3} and 0.6±0.5 μg m^{-3} (respectively) reflecting the BC and NO_x difference of about a factor of two higher during weekdays. Factor COA did not show statistically significant variation, (1.4±1.1 μg m^{-3} and 1.2±0.9 μg m^{-3}, for WD and WE, respectively). However, given the fact that AMS factor COA presents two peaks at about 12:00 and 20:00, further separation was required. Factor COA was divided into WD-WE periods, further split between day time (09:00-18:00) and evening time (18:00-24:00). COA-day was found to be about 25% higher during weekdays (1.03±0.78 μg m^{-3}) relative to weekend (0.76±0.41 μg m^{-3}), statistically different (t-test, 95%). HOA presented overall statistically significant lower values over weekend periods at both day and evening periods, with the former reduced more (about 60%) than the latter (about 20%).

4. DISCUSSION

4.1 Possible source attribution

The Cluster Ca-EC has previously been associated with primary traffic- related combustion particles in both laboratory (Toner et al. 2006), andfield measurements (Dall'Osto et al., 2009b, Toner et al., 2008), and this study is in agreement with its primary origin from vehicular emissions. Traffic markers such as NO_x and BC also show good correlation with cluster Ca-EC ($R^2 = 0.85$ and 0.7, respectively). Cluster OC presents features pointing towards a primary organic source, similar to cluster Ca-EC; it shows a strong organic carbon signature, a small aerodynamic diameter and peaks in the morning rush hour. However, the cluster OC was internally mixed with sulphate and was elevated also in the evening time. This suggests an additional source occurring in the evening, unlike the cluster Ca-EC which decreases during the evening. The morning peak probably arises from condensation of semi-volatile organic compounds onto pre-existing particles, and the evening peak may be due to condensation caused by reductions in air temperature. Cluster Na-EC-OC showed a broader size distribution with a greater proportion of coarser particles and a mass spectrum internally mixed with inorganic species including sodium and nitrogen, peaking during evening hours. Whilst this particle type contains the strongest peak at m/z 39, we exclude a biomass origin for a number of reasons. The peak at m/z 39 is not only associated with potassium ($[K]^+$ - to which the ATOFMS is especially sensitive), but may also be due to an organic fragment $[C_3H_3]^+$ (Silva and Prather, 2000). The complete absence of common peaks associated with the presence of potassium (i.e. m/z 113 $[K_2Cl]^+$ or m/z 213 $[K_3SO_4]^+$) and a ratio between m/z 39 and m/z 41 of about 18 (the isotopic ratio $^{39}K/^{41}K$ is 13.28) strongly suggest that the m/z 39 peak is not due to potassium alone, whereas it dominates in biomass combustion particle types, along with other potassium clusters (Silva et al. 1999). This particle type could originate from a number of sources occurring during the evening times but may also arise from physical processes occurring in the atmosphere during evening time when air temperature falls. During the summer of 2003, an ATOFMS was deployed in another European capital (Dall'Osto and Harrison, 2006) and most of the carbon-containing particles appeared to be a secondary product of atmospheric chemistry and one specific class peaked every night at 22:00, when lower temperature and increased RH values favoured condensation. The secondary particles showed clear internal mixing of organic and inorganic constituents in contrast to their common theoretical treatment as external mixtures. The cluster Na-EC-OC from this London field study shows similar mass spectral features, but does not show the expected diurnal variation.

The cluster SOA-PAH exhibits a unique set of properties, including weekday-weekend variation, maximum frequency during the warmest part of the day, and a mass spectral signature associated with PAH and oxygenated high molecular mass compounds. The fact that cluster SOA-PAH is detected predominantly during weekdays and presents a maximum during the midday hours suggests a photochemical mechanism linked with volatile organic compounds (VOC) arising from traffic activity. The weekday-weekend trend also suggest an anthropogenic source. The mass spectrum of cluster type SOA-PAH was compared with the ATOFMS particle mass spectral libraries. Source signatures, or mass spectral "fingerprints", were obtained by using ATOFMS data from a variety of sources (Toner, 2008). Cluster SOA-PAH did not match exactly any of the 20 different ART2a clusters representative of different cooking related sources, nor any oil, gasoline or diesel combustion source. Finally, it is important to note the absence of any peak associated with common metals (i.e. Ca, Na, K, V) detected in ATOFMS mass spectra of particles originating from primary anthropogenic aerosol sources. The temporal trend of the cluster SOA-PAH suggests that this particle type is short-lived, perhaps due to chemical decomposition. The ATOFMS mass spectrum shows signals usually associated with PAH components already described in section 3.1.1, which point to a primary aerosol source. However, the

PAH signature may be related to secondary components, possibly oxidation products of PAHs. Reactions of degradation products may also lead to further secondary compounds. Webb et al. (2006) for example showed the organic aerosol product formed from the photo-oxidation of o-tolualdehyde contained a diverse range of chemical functionalities including mono-aromatic, carboxylic and carbonyl groups which were inferred to be photochemical by-products but around 3% of the organic content resolved was polycyclic aromatic (PAH) in nature. The ATOFMS is very sensitive to polycyclic aromatic structures, so whilst PAH may be a minor component of the mass of the particle, they can generate a disproportionate fraction of the mass spectral signature. The cluster SOA-PAH does not behave as a typical semi-volatile species whose concentration increases as temperature decreases. The fact that its temporal trend does not correlate with any commonly identified primary aerosol components or markers (Ca-EC from ATOFMS, BC, NO_x, SO_2) excludes a primary aerosol source, and the maximum intensity at noon points towards a photochemical origin. Whilst PAHs are emitted directly from combustion processes, the sources of oxygenated PAH emissions in the atmosphere can be both by direct emission and by tropospheric conversion of PAHs, but quantitative data on the importance of secondary versus primary origins are scarce (Walgraeve et al., 2010). Ning et al. (2007) reported the daily variation in chemical characteristics of urban secondary ultrafine aerosols, showing that afternoon concentrations of oxygenated organic acids and sulfate rose relative to primary organic compounds in the morning and demonstrating that secondary photochemical reactions are a major formation mechanism of ultrafine aerosols in the afternoon. Specifically, the larger decrease in the concentration of non-oxidized PAHs and alkanes compared to CO in the afternoon indicated their possible volatilization and photo-oxidation in addition to dilution. Verma et al. (2009) suggested in a subsequent study that the photochemical transformation of primary emissions during atmospheric aging enhances the toxicological potency of primary particles in terms of generating oxidative stress and leading to subsequent damage in cells. Our study shows evidence of secondary reactions modifying the primary organic particles emitted in the morning rush hour.

As a wide range of chemical compounds is present both in the particle and gas phase compared to a controlled laboratory experiment, any chemical mechanism is highly speculative. However, by considering different sub-groups within cluster SOA-PAH, some insights can be gained. Figure 6 shows the difference in positive mass spectra between SOA-PAH particles with high and low peak area at m/z 81 ($[HSO3]^-$), an ATOFMS marker for particle acidity (Whiteaker et al. 2003, Pratt et al. 2009). SOA-PAH particle mass spectra with an absolute peak area lower than 2,000 are subtracted from those with absolute peak area greater than 10,000. The more acidic the particles (positive values, Figure 6), the more oxygenated peaks (m/z 43, 57, 69 and 81) along with peaks at m/z > 100 are seen. On the other hand, when the sulphuric acid content is very low (negative values, Figure 6) clear organo-nitrogen peaks (likely to be amines) can be seen in less acidic particles (m/z 39, 74 and 86 associated with organic-nitrogen species are present). Figure 6 suggests more acidic particles enhance secondary organic aerosol production (positive values). We interpret the higher amount of organo-nitrogen peaks in the less acidic particles as the reason for the reduced acidity. In other words, the organo-nitrogen species are the species responsible for the reduced acidity of this particle type.

4.2 Comparison with the AMS findings

The AMS instrument provides invaluable quantitative information upon the aerosol mass loading of generic organic components. In the last decade, the AMS non-refractory organic components have been sub-divided into two broad groups: hydrocarbon-like and oxygenated organic aerosol (HOA and OOA, respectively) (Canagaratna et al., 2007). Recently, Positive Matrix Factorization (PMF) has been demonstrated to be a powerful tool for the purposes of profiling different components of the ambient organic aerosol data matrix from the AMS. Lanz et al. (2007) and Ulbrich et al. (2009) for example reported a third AMS component: a less-oxygenated (relative to the factor OOA), semi-volatile organic aerosol that correlates well with nitrate and chloride. During this REPARTEE I experiment, Allan et al. (2010a) reported a detailed analysis of the AMS organic aerosol component sampled during the REPARTEE-I campaign, reporting three components: HOA (25%), OOA (53%) and a factor associated with primary organic aerosols related to cooking emissions COA (22%). This COA factor has also been recently reported in other large megacities (Huang et al. 201, Sun et al. 2011) but not compared with any other on line instrument. In this study we attempt to compare the AMS PMF factors (with particular emphasis on the COA) seen by the AMS with the on line measurements taken with the ATOFMS. Not only are ATOFMS particle type mass spectra correlated with the AMS factors, but also the temporal trend of a specific m/z peak (55, a m/z peak characteristic of the COA AMS factor) is also studied. A comparison between the ATOFMS and the AMS is not straightforward, as the qualitative temporal information of the ATOFMS particle number concentration of single particle mass spectral type does not allow a meaningful correlation with quantitative aerosol mass loading concentrations of organic components provided by the AMS. A correlation coefficient (R^2) matrix between ATOFMS particle types (number) and AMS mass concentrations appears in Table 2.

ATOFMS cluster Ca-EC, as well as cluster OC, correlate with the AMS HOA ($R^2 =$ 0.65 and 0.50 respectively), as shown in earlier studies (Drewnick et al., 2008). The AMS factor OOA represents a well-aged secondary organic aerosol, and was found consistent with an atmospheric regionally transported source rather than local meteorology, as reported in Dall'Osto et al. (2009a). It correlates weakly with particle type Na-EC-OC. Beside the commonly measured HOA and OOA factors, a further component, COA exhibited a unique mass spectrum with strong signals at m/z 41 and m/z 55. However, as noted by Allan et al. (2010b), the 3 factor solution approach tended to result in residuals larger than would be considered optimal according to the error model, which indicates that the number of factors used is insufficient to capture all of the chemical variability within the dataset. However, the fourth factor solution generated some splitting of PMF factors and therefore the three factor solution was kept.

This implies that the 3 factor solution is masking some additional information but the variability is not enough to justify the 4 factor solution or additional sources of organic aerosols rather than the three (HOA, OOA and COA). M/z 55 (a marker of COA) was found to have large variability (Allan et al. 2010b) but a 4-factor solution could not be justified.

The ATOFMS did not find any particle type associated with cooking activities. Some peaks usually attributed to cooking activities (Rogge et al. 1993) were found in clusterSOA-PAH. . Figure 2 shows peaks at m/z -256 (thought to be hexadecanoic acid) and m/z -284 (octadecanoic acid). Ning et al. (2007) reported ultrafine particles sampled in the afternoon in Los Angeles to show reduced nitrate concentrations (temperature increasing in the afternoon), to contain more organic matter than the morning samples (more SOA), to be more acidic (less ammonia to neutralize the sulphuric acid), and to be rich in octadecanoic acid and hexadecanoic acids. Whilst Rogge et al. (1993) showed that food cooking is a source of organic acids, it was concluded that atmospheric chemistry (oxidation of VOC precursor gases) is more likely responsible for their formation as food cooking alone cannot explain the atmospheric concentrations measured (Pandis et al., 1993; Rogge et al., 1993). However, far fewer published profiles are available for food cooking relative to motor vehicles and biomass combustion, and significant inconsistencies exist between the ambient data and published source profiles so further studies are required in order to correctly apportion food cooking emissions (Robinson et al., 2006).

The ATOFMS and the AMS rely on different ionization principles (laser desorption and electron impact, respectively), which inherently result in different fragmentation patterns. In the ATOFMS, m/z 55 is usually seen in organic aerosol with aromatic compounds (Prather and Sullivan, 2005) but a comparison between the same m/z seen by the two different instruments is still attempted. By querying all the ~150,000 ATOFMS single particle mass spectra containing a peak at m/z 55 (peak height >100), a key peak describing the third AMS factor (COA) solution (Allan et al. 2010a), 11,500 particles were found with such peak. Figure 7 shows the average ATOFMS mass spectra of particles containing a peak at m/z 55 (from here called particle type m/z 55). This peak does not seem to appear in inorganic particle types (Table 1). The average mass spectrum shows peaks due to OC (m/z 27, m/z 41, m/z 55, m/z 63, m/z 77), fragments of large aromatic compounds (m/z 115, m/z 165), nitrate (m/z -46, m/z -62) and sulphate (m/z -97), all peaks contained within particle types OC, Na-EC-OC and SOA-PAH. The broad similarity of the mass spectra shown in Figure 7 with particle types OC, Na-EC-OC and SOA-PAH is also reflected in the fact that the total number of particles containing m/z 55 broadly follows the sum of the 3 ATOFMS Art-2a clusters (Figure 4). The temporal trend of particle type m/z 55 in Figure 5e, where a bimodal diurnal profile can be seen peaking at noon and during evening times bears some similarity to the COA factor, but the correlation between the sum of the three ATOFMS types (OC + Na-EC-OC and SOA-PAH) and AMS factor COA is entirely insignificant ($R^2<0.1$) (Table 2). It does however raise the question over whether the COA factor is comprised of a number of different particle types arising from different sources. The two instruments involve very different vaporisation/ ionisation procedures (ATOFMS by u.v. laser and AMS by heating and electron impact) probably leading to significantly different mass spectral fragmentation patterns in terms of relative peak intensities, if not m/z values. The cooking aerosol may be transparent to the u.v. laser, hence failing to ionise in the ATOFMS. The ATOFMS analyses individual particles and therefore sees a particle resulting from coagulation as different from its two parent particles whereas the AMS views an aggregate mass spectrum of particles of all types admitted to the instrument at a specific time. It should also be remembered that the two instruments are responsive to different particle size ranges and that the cooking oil aerosol characterised as the COA factor by the AMS may be of two small a size (< 200 nm) to be seen by the ATOFMS. These differences make it very difficult to try to intercompare data from the two instruments, although sometimes data from one can be valuable in informing interpretation of data from the other (e.g. Dall'Osto et al., 2009a; Drewnick et al., 2008). In this dataset, the ATOFMS does not appear to see any particle type characteristic of a cooking source.

5. CONCLUSION

This work emphasises that neither the AMS nor the ATOFMS alone is able to give a comprehensive insight into aerosol composition and sources. Our earlier work has demonstrated that in combination they give far greater insights into aerosol behaviour than either technique can alone (Dall'Osto et al., 2009a,b).. The AMS has a well proven capability to quantify generic source-related categories of non-refractory aerosol. The ATOFMS gives mass spectral information upon individual particles which, even after clustering particles with similar size distribution and mass spectral characteristics, presents information which can be very difficult to interpret in relation to the sources or atmospheric processing, as is the case with some particle types identified in this study.

The ATOFMS cannot provide quantitative aerosol mass loading concentrations, but its unique strength relies in the fact that it can monitor in real time variations in the single particle composition. Further work is needed in order to attribute mass spectra to particular sources with greater confidence. Comparing laboratory and ambient spectra may not be sufficient to associate a specific mass spectrum to an aerosol source seen in the ambient data, as particles with primary and secondary origins may have broadly similar mass spectra, and particles are modified substantially during atmospheric transport processes. The ATOFMS particle types Ca-EC, which derives from road traffic, and OC, containing organic carbon from primary sources, correlate strongly with the AMS HOA factor. The modest correlation between ATOFMS particle Na-EC-OC and AMS OOA suggests that this is an aged particle type containing mainly secondary organic carbon. ATOFMS type SOA-PAH appears to be a specific component of secondary organic aerosol for which the ATOFMS has high sensitivity, but which does not represent the temporal trends in total secondary aerosol as shown by AMS factor OOA. There is no clear evidence that any ATOFMS particle type, or combination of particle types, corresponds to the AMS COA cooking factor.

PMF analysis on the AMS datasets is revealing new features in the organic components of the aerosols and it is proving to be an excellent tool for extracting information from the AMS mass spectra. It is imperative not only to justify PMF solutions mathematically, but also by comparing different AMS PMF solutions with external data such as can be provided by the the ATOFMS. This study shows that the urban organic aerosol is complex and unfortunately the correlations between the two mass spectrometers have prove to be rather weak. Yet, it is very likely that the PMF analysis with the recent High Resolution HR-Tof-AMS (DeCarlo et al. 2006) of organic matrices in the future will generate more than the common 3-4 factors seen with lower resolution AMS mass spectrometers. We continue in our belief that it is important to continue deployment of different on line particle mass spectrometers to reduce uncertainties in the source apportionment of the aerosols.

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TABLE CAPTIONS

Table 1. ATOFMS particle clusters identified from the REPARTEE campaign.

Table 2. Correlations (R^2) between ATOFMS organic particle types (number) and AMS concentrations averaged over 3-hour intervals.

FIGURE CAPTIONS

Figure 1. Positive and Negative ART-2a area vectors attributed to (a) Ca-EC, (b) OC, (c) Na-EC-OC and (d) SOA-PAH

Figure 2. Single particle positive and negative mass spectra of an individual particle belonging to ART-2a cluster SOA-PAH.

Figure 3. Size distributions of the 4 ATOFMS particle types described in Figure 1

Figure 4. Temporal trends of (a) ATOFMS clusters described in figure 1, (b) BC and nitrogen gases and (c) AMS profiles as reported in Allan et al. (2010).

Figure 5. Figure 5. Average diurnal profiles for (a)ATOFMS cluster described in Figure 1, (b) AMS PMF factors as reported in Allan et al (2010); (c) ozone, NO_x and black carbon concentrations; (d) relative humidity and temperature and (e) ATOFMS hit particles with m/z 55 (peak height > 100).

Figure 6. Positive and negativeART-2a area vectors differences for the positive mass spectra (cluster SOA-PAH with high content HSO_3^- and little content; peak area m/z -81>10,000 and m/z -81< 2,000 respectively).

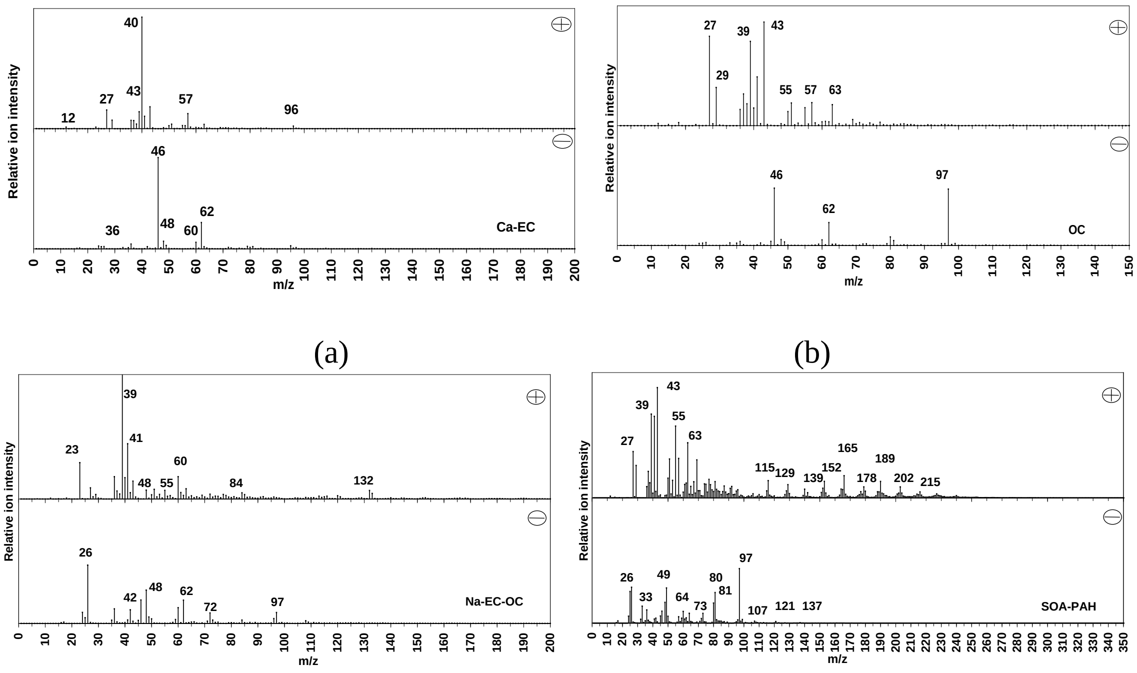
Figure 7. Average mass spectra for all hit particles during the REPARTEE I campaign containing values of peak height at m/z 55 higher than 100.

Table 1. ATOFMS particle clusters identified from the REPARTEE campaign

Main	ATOFMS cluster	N particles	% cluster	Particle description
Secondary OA	LRT nitrate	43516	33.7	Long range transport aerosols (Dall'Osto et al. 2009a)
	LRT core	10278	8.0	
	Local nitrate	29563	22.9	
	Amine	2306	1.8	
	HMOC (fog)	4865	3.8	Secondary organic aerosol during fog (Dall'Osto et al. 2009b)
	MSA (fog)	245	0.2	
	SOA-PAH	2834	2.2	This study
Primary OA	Ca-EC	5496	4.3	This study
	OC	4671	3.6	This study
	PAH	269	0.2	This study
	EC	2001	1.5	Coarse Elemental Carbon Long range transport aerosols (Dall'Osto et al. 2009a)
	Na-OC-EC	2207	1.7	Inorganic particles due to sea salt (NaCl) and Fe (mainly during long range transport)
Inorganic	NaCl only	3637	2.8	
	Aged NaCl	15638	12.1	
	Fe	1748	1.4	
	TOTAL	**129274**	**100.0**	

Table 2. Correlations (R^2) between ATOFMS organic particle types (number) and AMS concentrations averaged over 3-hour intervals.

3 hour resolution	AMS OOA	AMS HOA	AMS COA	AMS org
ATOFMS Ca-EC	<0.1	0.65	<0.1	0.12
ATOFMS OC	<0.1	0.50	<0.1	0.14
ATOFMS Na-EC-OC	0.35	-0.1	<0.1	0.14
ATOFMS SOA-PAH	<0.1	<0.1	0.15	<0.1



(a) (b)

(c) (d)

Figure 1. Positive and negative ART-2a area vectors attributed to particle types (a) Ca-EC, (b) OC, (c) Na-EC-OC and (d) SOA-PAH

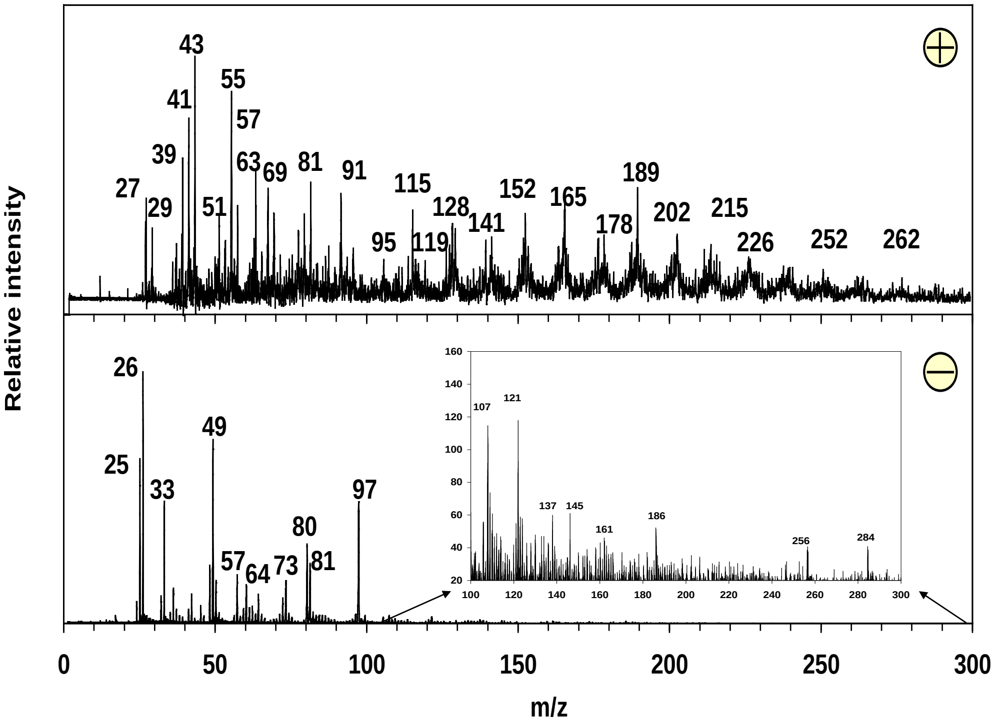


Figure 2. Single particle positive and negative mass spectra of an individual particle belonging to ART-2a cluster SOA-PAH.

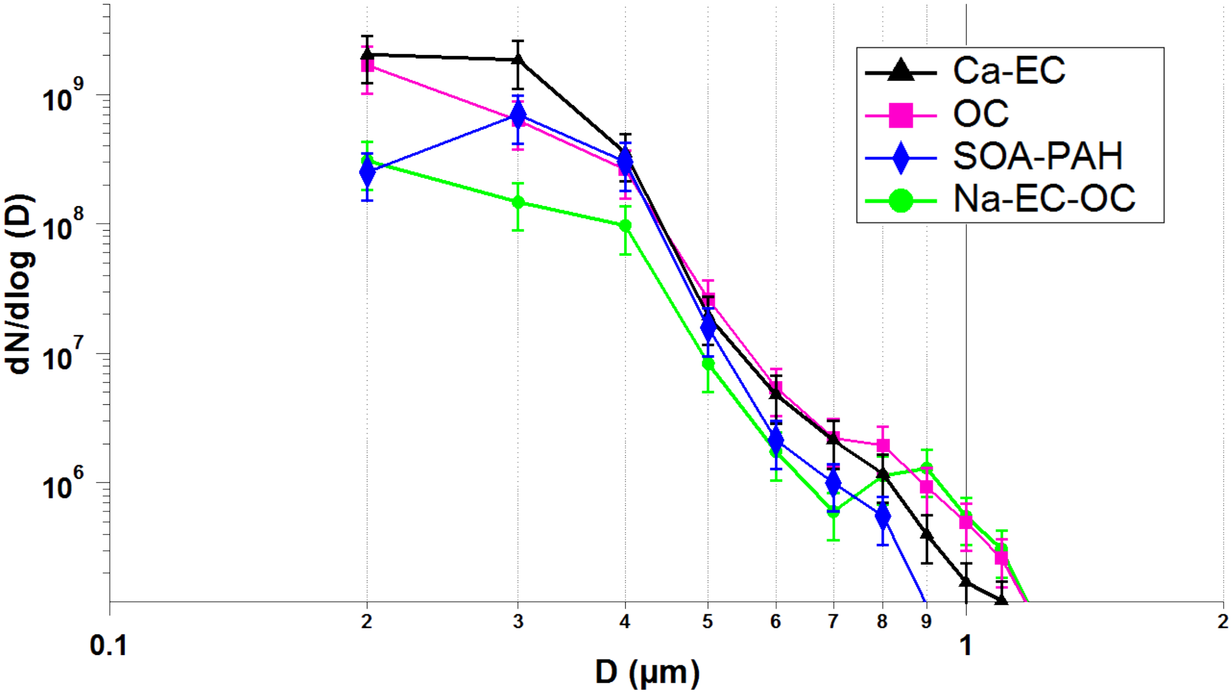


Figure 3. Size distributions of the 4 ATOFMS particle types described in Figure 1

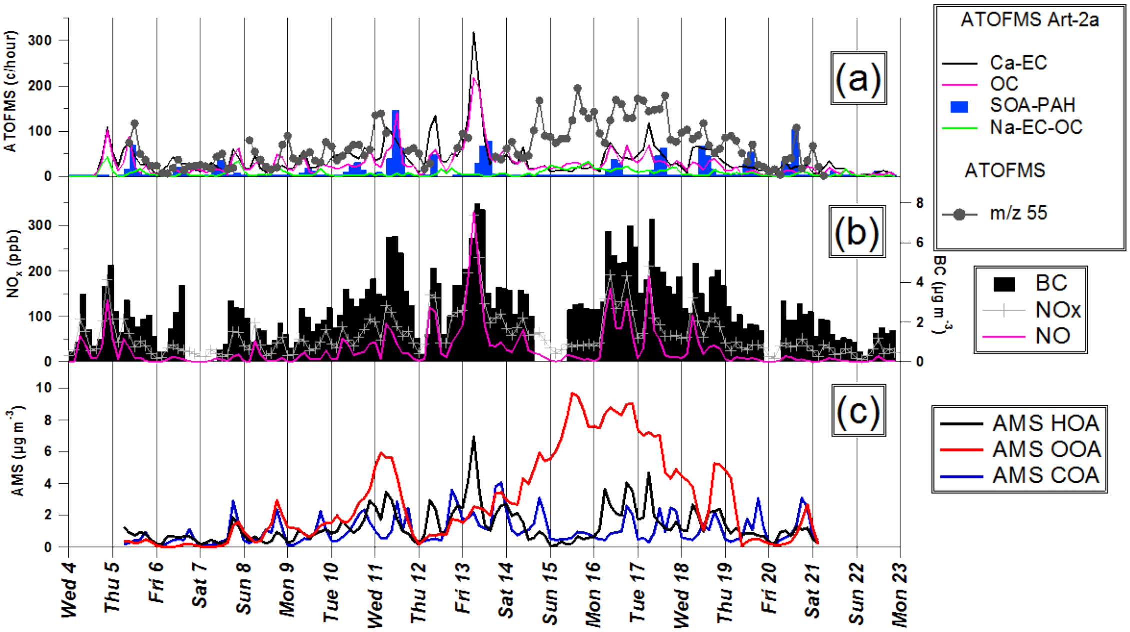
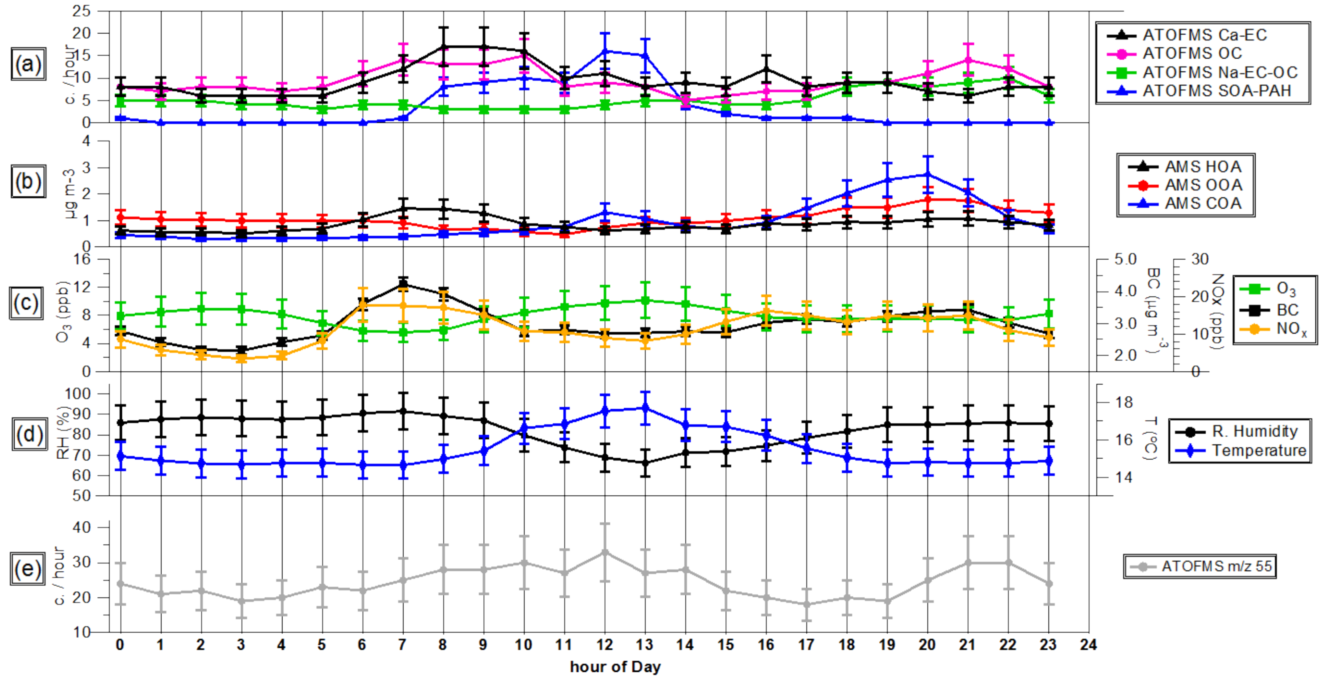


Figure 4. Temporal trends of (a) ATOFMS clusters described in Figure 1 and ATOFMS m/z 55, (b) BC and nitrogen gases and (c) AMS PMF factors as reported in Allan et al (2010).



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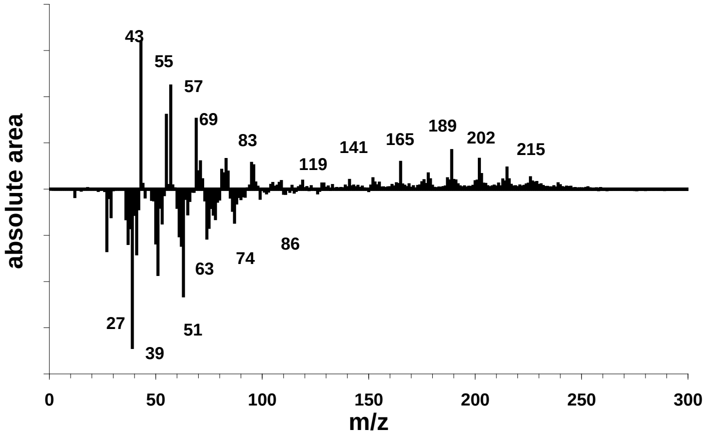

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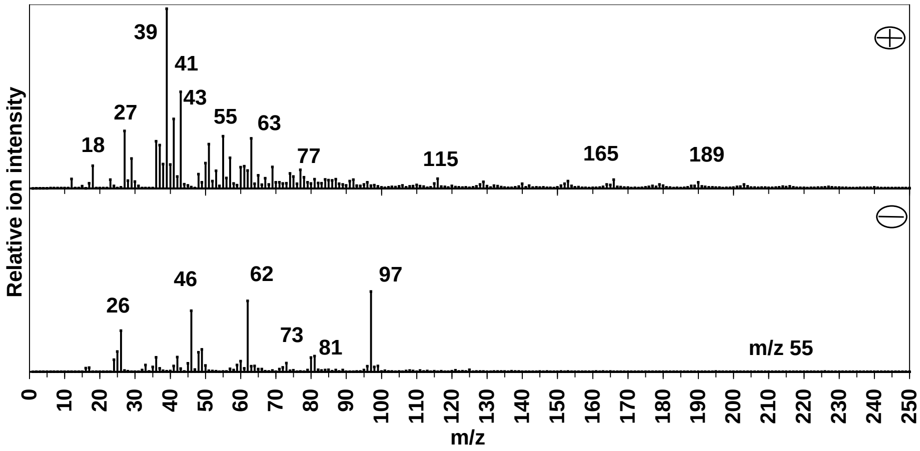

Figure 7. Average mass spectra for all hit particles during the REPARTEE I campaign containing values of m/z 55 with peak height than 100.